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Energy Storage and Management in Supercapacitors for application in Piezoelectric Energy Harvesting Systems

Shashank Sripad[1], S. Jayanth Kumar[2], Anjana Jain[2]*

[1]Department of Chemical Engineering National Institute of Technology Karnataka, Surathkal – 575 025; India
[2]National Aerospace Laboratories, Bangalore, India – 560 037;

Abstract: Electrical double layer capacitors (supercapacitors) were fabricated using activated carbon as the active material and polyvinylidine fluoride (PVDF) as a binder with a suitable conductive additive (MWCNTs) together in an optimized ratio. The supercapacitor cells were assembled using an aqueous solution of 0.5M Na_2SO_4 as the electrolyte. These cells had an average capacitance of 1.7F each as measured by the constant current charging method. The two electrode symmetric cell had a specific capacitance of 23.05 F/g. The fabrication methodology has been discussed as well as the potential applications of the supercapacitor in piezoelectric element based energy harvesting systems have been elucidated.

Introduction

Electrical double layer capacitor (EDLC), sometimes called a supercapacitor or an ultracapacitor, stores electric charge in the electrical double layer at a surface-electrolyte interface, primarily in high-surface-area carbons. Because of the high surface area and the thinness of the double layer, these devices can have very high specific and volumetric capacitances and essentially unlimited charge/ discharge cycle life[1].

Supercapacitors have a much higher (at least one order of magnitude higher) power density and higher shelf-life than batteries. At the same time they have a considerably lower energy density[2]. Conventional electrolytic capacitors on the other hand have a much higher power density and much lower energy density compared to supercapacitors. This makes supercapacitors a bridge between capacitors and batteries as illustrated by the Ragone plot in Figure 1.

Energy harvesting circuits have a very low power output; sufficient energy must be accumulated to make the setup feasible for any practical use. Also, on inclusion of an energy storage device, it is important to ensure shortercharging duration so that the system doesn'tremain dormant for longer durations. These factors interlocked with sufficiently long cycle life are the essential elements of an effective energy harvesting system.

Rechargeable batteries are usually rated with a cycle life of about 300-1000 cycles[3] while supercapacitors are rated higher than 100,000 cycles. Supercapacitors can be charged at any voltage up to their rated voltage while batteries have to be charged at a small voltage window around their rated voltage. This aspect defines the charging characteristics of a storage device in an energy harvesting circuit.

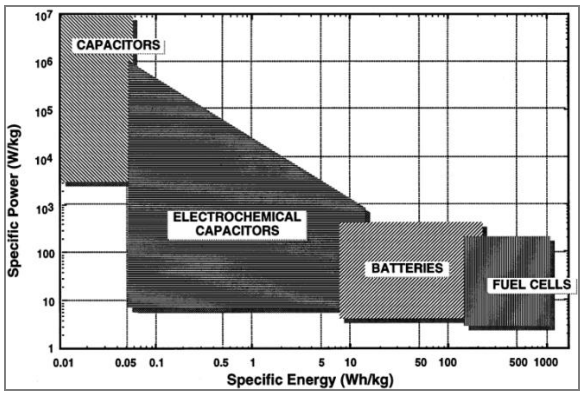

Figure 1. The Ragone plot given above illustrates how supercapacitors form a bridge between capacitors and batteries with intermediate energy density and power density[4].

Energy harvesting systems which employ piezoelectric elements as micropowergenerators utilize the direct piezoelectric effect wherein certain materials transform mechanical strain to electrical charge[5].They have three essential parts namely the micropowergenerator, the voltage rectifier and the energy storage/ management device. Such systems are known to have low power and a varying voltage depending on the mechanical input and often require several adjustments in circuitry like adjusting the rectifier output voltage to obtain maximum efficiency[6].

The presence of mesopores in electrodes based on CNTs, due to the central canal and entanglement enables east access of ions from electrolyte. For electrodes built from multiwalled carbon nanotubes (MWCNTs), specific capacitance is in a range of 3-135 Fig[7, 8].

The following study includes, firstly, a simple procedure to fabricate activated carbon based supercapacitors, secondly, a basic testing scheme for the supercapacitor cell and lastly, application of the supercapacitor cells in a piezoelectric microgenerator based energy harvesting system. The objective of this study is to study feasibility of using supercapacitors along with piezoelectric micropower generators to form an effective energy harvesting setup.

Experimental

Fabrication of the supercapacitor

The basic schematic of a supercapacitor given in Figure 2 shows a current collector onto which the active material of the electrode is deposited. Two such electrodes are separated by a separator to prevent electrical contact.

This setup is immersed in an electrolyte solution which furnishes ions. During the charging process the ions of the electrolyte migrate towards the electrodes and cling on to form the Electrical Double Layer where the charge/ energy is stored.

a) Current collector: Aluminium foil which was used as a current collector had a thickness of 0.05mm and was subjected to mechanical etching to improve the adhesion of the deposit. After the etching process the foil was fixed in a mould of suitable dimensions for the deposition process

b) Electrode: Activated carbon is the most easily accessible and is also inexpensive which made it a suitable choice for the supercapacitor electrode.

The electrodes prepared were mainly based on activated carbon 64.57% wt. with MWCNTs 6.08% wt. functioning as a conductive additive and 29.35% wt. of PVDF as a binder**.**

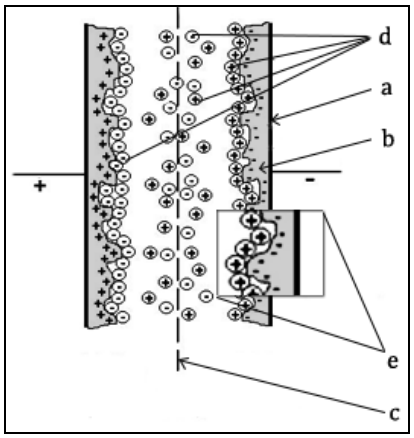

Figure 2.The schematic diagram of an EDLC[9]. a. Current collector b. Active material c. Separator d. Ions of the electrolyte solution e. Electrical double layer

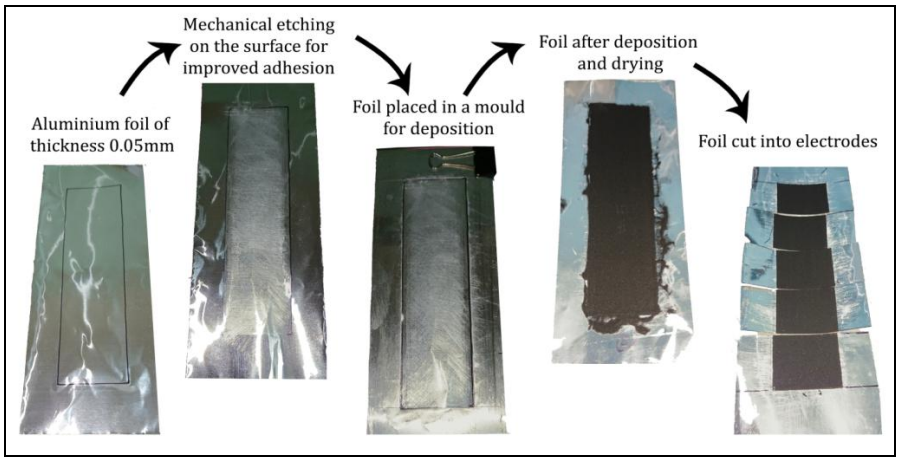

Figure 3.Flowchart of the electrode fabrication process.

PVDF was dissolved in the solvent Dimethylformamide (DMF) after which activated carbon was added to it and stirred for a suitable duration. A certain quantity of Carbon nanotubes (CNT) was separately dispersed in DMF. These two solutions were mixed to form slurry which was then deposited onto the aluminum foil. The foil was then dried in a furnace to evaporate the DMF solvent. The entire process of preparation of the electrodes is illustrated via a 'flow chart' in Figure 3.

c) Separator & Electrolyte: A suitable ion permeable separator was used to prevent electrical contact between the electrodes.Aqueous electrolyte was chosen for low cost, high safety, long lifetime & low resistance[10].

Na2SO4 in an aqueous solution was chosen due to its superior performancecompared to other aqueous electrolytes[11]. An aqueous solution of 0.5 M Na2SO4 was used as the electrolyte due to which the maximumcell voltage is limited to 1.2V; which is the decomposition voltage of water.

The cells were fabricated using 3cm x 4cm electrodes cut from the foil and placed on the two sides of a filter paper separator and then sealed in a plastic cover in flat plate design;the ends of the Aluminum foil functioned as leads which protrude from the cover. This stack was injected with the electrolyte using a syringe.

SEM & XRD study of the surface of the electrodes

SEM images were obtained using JEOL scanning electron microscope and XRD patterns are recorded with Bruker X-ray diffractometer using Cukα2 radiation with graphite monochromator. The diffraction pattern in the 2θ range of 10 to 60^o is recorded and the sample is rotated at the scan speed of 1^o/minute.

Testing the supercapacitor

The supercapacitor was tested using the constant current charging method and its capacitance was subsequently calculated. Several trials were conducted and the average capacitance was calculated.

An electrochemical impedance spectroscopy analysis was also conducted and the real part of the capacitance was plotted against frequency.

Results and Discussion

SEM & XRD of the electrode surface

SEM images in Figure 4 show the characteristic surface of the electrode and reveal the porous structure of the activated carbon composite. This highly porous structure provides a high surface area which is responsible for the high capacitance of the electrode.

XRD pattern shown in Figure 5, displays peaks at 29.46^{o} which can be attributed to activated carbon, at 26.70^{o} is that of carbon nanotubes and the sharp peaks at 38^{o}& 45^{o} are those of the aluminum current collector.

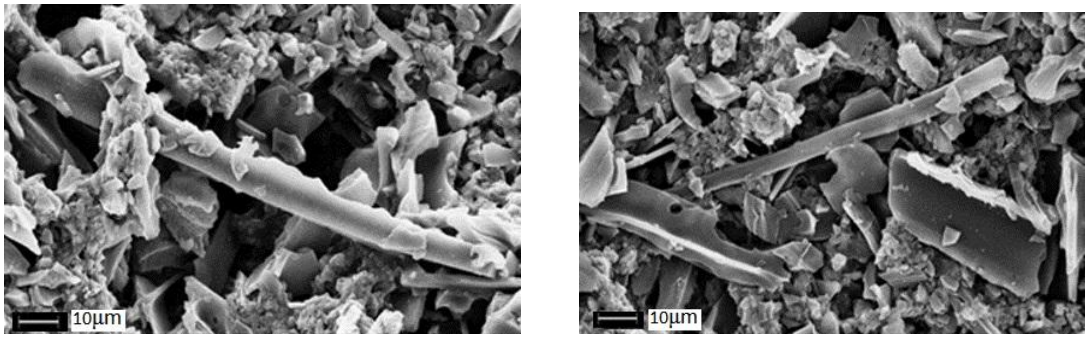

Figure 4. SEM images of the electrode surface

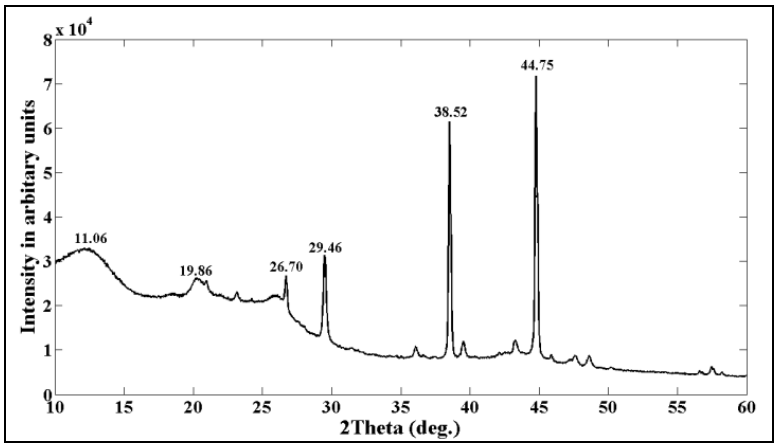

Figure 5. XRD Pattern of the electrode

Constant current charging results

A supercapacitor is essentially two capacitors in series, one at each of the electrodes. So if the capacitance at each electrode due to the double layer is C_{dl}, the capacitance of the supercapacitor cell C_{cell} can be given by,

$$C_{cell} = \frac{C_{dl}}{2} \dots (a)$$

The specific capacitance C, of each cell can be calculated using m_{AC}, the mass of the active material on the electrode,

$$C = \frac{C_{dl}}{m_{AC}} \dots (b)$$

The basis for the constant current charging method lays in the following relationship between current I and the rate of change of voltage V,

$$C_{cell} = \frac{I}{dV/_{dt}} \dots (c)$$

Sample charging curves are shown in Figure6, for a constant current of 0.01A and the change of voltage with respect to time is seen. The slope of this plot yields the rate of change of voltage which when used in equation (c) gives the capacitance of the cell. The average capacitance exhibited by the sample cell fabricated using (3x4) cm^2 electrodes was calculated to be 1.7F.

Using equation (a) the corresponding double layer capacitance at each electrode can be calculated and subsequently using the mass of active material in equation (b) the specific capacitance can be calculated. The specific capacitance of the electrode in the same cell turns out to be about 32.92 F/g.

The energy density E and the power density P of a supercapacitor is given by,

$$E = \frac{\frac{1}{2}CV^2}{W} \ldots (d)$$

Where C is the capacitance of the supercapacitor, V is the maximum rated voltage, W is the weight of the device. The supercapacitor fabricated had an energy density of 0.8 Wh/kg.

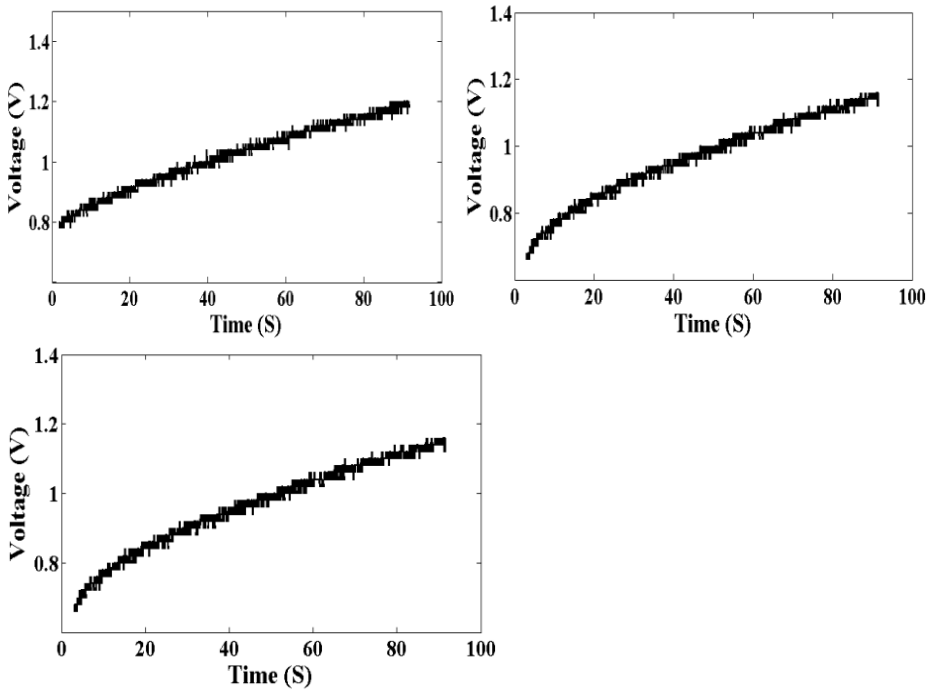

Figure 6. Constant current charging curves of the supercapacitor.

Constant current charging curves which show the variation of voltage with time at a constant current of 0.01A. This gives the charging characteristics as well as the charging capacitance.

Electrochemical impedance spectroscopy:

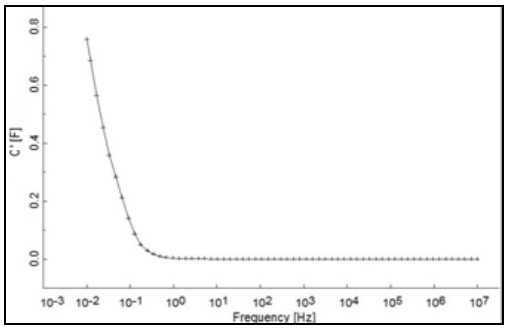

Figure 7. Electrochemical impedance spectroscopy

As shown in Figure 7, an electrochemical impedance spectroscopy analysis was carried out to measure the real part of the capacitance against frequency. The real part of the capacitance measured also characterizes

the energy storage capability of the supercapacitor and the graph is a typical characteristic graph of an activated carbon supercapacitor[12].

Application in Energy Harvesting

The supercapacitor fabricated can be used either as a primary energy storage device or as a buffer to manage the harvested energy.

Piezoelectric elements function as low power generators and supercapacitors can be easily coupled with such elements to form an energy harvesting setup.

The supercapacitor fabricated is well suited to be used with thin film piezoelectric devices which give a micropower output as developed in a previous study[13]. Figure8 shows the experimental setup of the energy harvesting system featuring the supercapacitor and a thin film piezoelectric microgenerator (fabrication is discussed elsewhere)[14] which works on application of constant pressure.

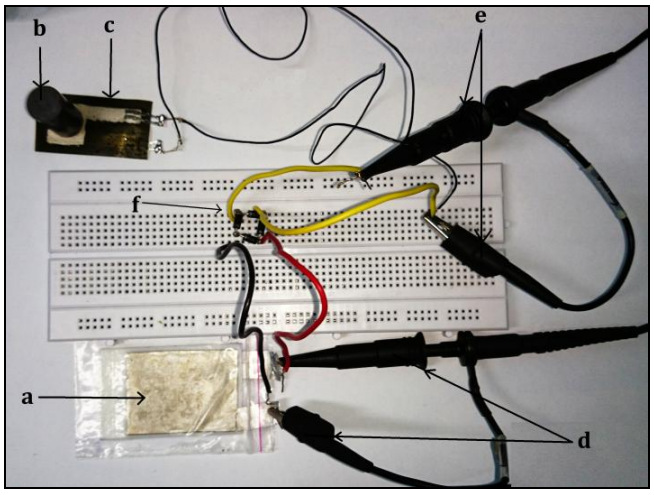

Figure 8. Energy Harvesting Setup a. Supercapacitor b. Point of application of the mechanical input c. Piezoelectric element d. Supercapacitor voltage measurement e. Rectifier input measurement f. Rectifier circuit

On application of a mechanical load weighing 1.85 kg at point b. in Fig 7 for a sufficient duration, the supercapacitor was charged to a voltage of 0.57V which is the maximum rectifier voltage output of the piezoelectric element. The maximum voltage can be increased up to 1.2V by using different piezoelectric materials.

This setup finds application in places where the piezoelectric element generates power through either ambient vibrations around the setup or constant pressure on the setup. The energy so harvested can be used to power lighting systems, microelectronic circuits and other such devices.

In conclusion, a feasible and effective energy harvesting setup has been constructed using a supercapacitor with a piezoelectric micropower generator connected using a rudimentary bridge rectifier circuit.

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